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3,023,192 SEGMENTED COPOLYETHERESTER ELASTOMERS

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This application is a continuation-in-part of my copending application Serial No. 551,460, filed December 6, 1955, now abandoned, which is a continuation-in-part of application Serial No. 502,508, filed on April 19, 1955, and Serial No. 329,114, filed December 31, 1952, now both abandoned.

This invention relates to linear copolyesters and especially to elastomers prepared from compositions of certain polyester-forming components. More particularly, this invention relates to elastic fibers and films and similar shaped structures prepared from such copolyesters.

Most fiber-forming synthetic materials which have been proposed for replacement of rubber have fallen short, especially in the rate and degree of elastic recovery from deformation frequently referred to as "snap." For the purposes of this invention high elastic recovery is defined as being of the order of 90% or better within one minute after the tension has been released from the sample which has been elongated 50% at the rate of 100% per minute and held at 50% elongation for one minute. Stress decay is defined as the percent loss in stress in a yarn one minute after it has been elongated to 50% at the rate of 100% per minute.

For applications in textile and allied fields natural or synthetic rubber possess a number of disadvantages which tend to offset its desirable elastic properties. For example it cannot be used in garments without having its strands covered with such materials as cotton, or rayon, because of its unpleasant and undesirable effects when in contact with skin. It is colored, possesses an unpleasant odor, and is subject to deterioration under the influence of light and/or oxygen and rapidly loses its strength and elasticity. It is, therefore, desirable to find a new material which is highly elastic and has a higher modulus than rubber but which does not possess the undesirable characteristics of rubber. Elastic filaments and fibers having overall properties superior to those of rubber would occupy a place of considerable importance in the field of textiles and the like.

An object of this invention, therefore, is to provide a synthetic material capable of being formed into filaments, film and like structures which will possess high elastic recovery. Another object is to provide a synthetic filament- and film-forming polymer having the high elastic recovery characteristics of rubber, but which is substantially free of the disadvantages that rubber has in the textile field. Another object is to provide a process for preparing these polymers. These and other objects will be evident from the following discussion.

The objects of this invention are accomplished by providing a segmented or ordered copolyetherester comprising about 25% to about 65% by weight of segments of an aromatic polyester which melts above 200° C. in the fiber-forming molecular weight range (i.e., when the chain length of the polymer is sufficient for it to have a molecular weight of at least about 5,000) and about 35% to about 75% by weight of polyetherester units or segments prepared from difunctional polyethers having molecular weights in the range of approximately 350–6,000. This description of the invention is not intended to imply or require that the aromatic polyester segment of the copolymer actually have a molecular weight greater than 5,000, but is intended to mean that the aromatic ester portion present must be a segment (contain one or more repeating units) of a polymer which melts above 200° C. when its molecular weight is high enough for it to be fiber-forming.

These products have elastic recoveries of the order of 90% or better and stress decays below about 25%. Polyesters are prepared by condensing two small molecules to form a repeating unit of a polymer. Substantially all (i.e., above about 95%) of the repeating units of the polyester portions of the copolymers of this invention must contain an aromatic ring, which may be derived from an aromatic dicarboxylic acid in which the carboxyl groups are attached directly to the aromatic ring or from a bis-phenol. In either case, the ester linkages are attached directly to an aromatic ring. The preferred aromatic polyester segments of the copolyesters of this invention are prepared from aliphatic glycols and symmetrical aromatic dicarboxylic acids or their ester-forming derivatives.

The copolyetheresters of this invention are prepared by reacting one or more dicarboxylic acids or their ester-forming derivatives, one or more difunctional polyethers with the formula:

$$HO(RO)_nH$$

(in which R is one or more divalent organic radicals and n is an integer of a value to provide a glycol with a molecular weight of between about 350 and about 6,000), and one or more dihydroxy compounds selected from the class consisting of bis-phenols and lower aliphatic glycols with the formula:

$$HO(CH_2)_aOH$$

(in which a is 2–10), with the proviso that the reactants be selected so that substantially all of the repeating units of the polyester contain at least one aromatic ring. The resulting ester is then polymerized.

The reaction may be carried out in bulk or in a solvent medium which dissolves one or both of the reactants.

The preferred method for preparing these copolyether esters is to subject to an ester interchange reaction, followed by polymerization, one or more ester-forming derivatives of aromatic dicarboxylic acids in which the carboxyl groups are attached directly to the aromatic ring, one or more difunctional polyethers with the formula:

$$HO(RO)_nH$$

(in which R is one or more divalent organic radicals and n is an integer of a value to provide a glycol with a molecular weight of between about 350 and about 6,000), and one or more lower aliphatic glycols with the formula

$$HO(CH_2)_aOH$$

(in which a is 2 to 10).

Representative difunctional polyethers which may be used include the poly(alkylene oxide)glycols, such as poly(ethylene oxide)glycol, poly(propylene oxide)glycol, poly(tetramethylene oxide)glycol, poly(pentamethylene oxide)glycol, poly(hexamethylene oxide)glycol, poly(heptamethylene oxide)glycol, poly(octamethylene oxide)glycol, poly(nonamethylene oxide)glycol, and poly(decamethylene oxide)glycol; the dicarboxymethyl acids of poly(alkylene oxides), such as the one derived from poly(tetramethylene oxide)

$$HOOCCH_2(OCH_2CH_2CH_2CH_2)_xOCH_2COOH$$

or their esters; polydioxolane and other polyformals prepared by reacting formaldehyde with other glycols, such as pentamethylene glycol, or mixtures of glycols, such as a mixture of tetramethylene and pentamethylene glycols. Mixtures of glycols may also be used to prepare copolyethers, e.g., one which would have both ethylene oxide and tetramethylene oxide units in the polyether chain.